

## Influence of process variables on chemical devulcanization of sulfur-cured natural rubber



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### ABSTRACT

Chemical devulcanization of sulfur cured natural rubber (NR) was investigated using benzoyl peroxide (BPO) as a devulcanizing agent. The influence of important reclaiming parameters such as reaction time, reaction temperature and concentration of the devulcanizing agent on the devulcanization process and mechanical properties of the resulting products were studied. At devulcanization reaction time of 2 h (instead of 4 h) and lower concentrations of the devulcanizing agent selective scission of sulfur crosslinks were observed, however, both longer of the reaction time and higher concentrations of the devulcanizing agent process resulted non-selective chain scission. Mechanical properties of the devulcanized and redevulcanized samples using 6 phr of BPO, with different reaction times and temperatures were also investigated. Longer reaction time led to lower crosslink density which in turn caused tensile strength and elongation at break to decrease significantly. Likewise, higher reaction temperature accelerated scission of network crosslinks and resulted lower tensile properties. Blending of 40 wt% of the virgin rubber with the devulcanized one in the compound had no adverse effect on the scorch and optimum cure time and also does not extremely deteriorate the mechanical properties of the virgin rubber. This provided an effective route for chemical devulcanization of NR.

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## 1. Introduction

Management and recycling of crosslinked waste rubber is a serious problem of our society. Since polymeric materials do not decompose easily, disposal of these materials is a serious environmental issue [1]. Production of sulfur crosslinks between the rubber molecules by the process of vulcanization generates three dimensional network which needs a very long time for natural degradation [2,3]. Therefore, there are two problems; loss of valuable rubber besides environmental pollution, which gets the attention of academic and industrial centers towards revival of these materials after service period. Various techniques have been

proposed for recycling of waste rubber including chemical method [4], rubber incineration for production of energy [5], grinding and using rubber powder in civil engineering [6,7] or as filler in rubber and plastics [8–10] or for blending with raw rubber [11,12]. One of the most effective methods for reusing of waste rubber is devulcanization which includes scission of intermolecular bonds (C–S and/or S–S) resulting in shorter polymer chain with lower rubber properties [13]. In general, devulcanization can be performed in three different ways [14] including, physical, chemical and biotechnological processes [15,16].

In physical process, rubber is devulcanized with the aid of external energy such as mechanical and by means of two roll mill [17,18], microwave [19,20] and ultrasonic [21,22] forces. But these processes result in non-selective scission of crosslinks and main backbone's carbon–carbon bonds and thereby decrease the rubber quality after redevulcanization [14].

In chemical process, which is the preferred method in many industrial plants over the other mentioned options, various

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reclaiming agents like organic disulfides and mercaptans [23,24], and inorganic compounds [25–27] can be used for production of devulcanized rubber. The first step is swelling of rubber in organic solvents like toluene, or benzene, however, removal of these solvents after reaction is a serious challenge which also impose serious economic and environmental issues [1]. Supercritical fluids are the best substitutes for harmful solvents which are commonly used in different industries. Supercritical CO<sub>2</sub> is a cheap, non-flammable and non-toxic material and it can be removed from the polymer very easily, at the end of the process. This green devulcanization process was studied by some authors and reported as an effective chemical reclaiming method [28–30].

Masaki and co-workers devulcanized sulfur cured nitrile butadiene rubber in nitrobenzene at 200 °C for 3 h [31]. Roj et al. used benzoyl peroxide as a devulcanizing agent in order to devulcanize sulfur cured natural rubber by chemical and mechano-chemical techniques. Their results showed that selective scission of sulfur crosslinks occurs at low temperature (80 °C) and maximum reaction time (6 h) [32]. Devulcanization of styrene butadiene rubber on the basis of controlled oxidation with nitric acid was investigated by Rios and co-workers. They have shown that nitric acid expedites devulcanization reaction by oxidation of both sulfur crosslink and main chain resulting in forming COOH and NO<sub>2</sub> groups [33]. The ideal devulcanization process should be a combination of depolymerization, oxidation and crosslink scission without main chain scission [34].

The main objective of this study is to determine the optimum concentration of BPO needed for chemical devulcanization of sulfur cured natural rubber and to investigate the effects of the process variables including devulcanization time and temperature on the mechanical properties of the resultant materials. Degree of the devulcanization has been evaluated by measurement of the crosslink density of the reclaimed rubber using volume fraction of the rubber after swelling and sol–gel content and mechanical properties are evaluated through tensile measurements.

## 2. Experimental

### 2.1. Materials

Natural rubber (115-L (SMR)) was supplied by Baspar Sazeh Toos Co. Mashhad, Iran. The properties of this rubber are shown in Table 1. BPO as the devulcanizing agent and xylene as the solvent for chemical devulcanization were purchased from Merck Chemical Co., Germany. Toluene and acetone were supplied by Iran Petrochemical Co. (Arak, Iran) and used as solvent for characterization.

### 2.2. Chemical devulcanization process

Devulcanization process by means of xylene as the solvent and benzoyl peroxide as the devulcanizing agent was carried out in an oven. Xylene (boiling point: 139 °C) is a suitable solvent for such a high temperature reaction. The cured rubber sheet (20 g) with various amount of benzoyl peroxide and appropriate amount of xylene were kept in the oven at constant temperature. The amount of solvent should be sufficient to keep the rubber sheet submerged in the solvent (approximately 100 ml in our case). Devulcanization was carried out using 4 different concentrations

of BPO (0, 2, 4, 6 and 8 phr) for 2 h at constant temperature (80 °C). The effect of the devulcanization time (2 and 4 h) was investigated on the sample devulcanized with optimized amount of BPO. Finally, the effect of reaction temperature (80 and 110 °C) was studied on the sample devulcanized at optimum BPO level and maximum reaction time. Mechanical properties of the devulcanized rubber samples were determined in tensile test and compared with the original rubber.

### 2.3. Revulcanization process

The sheet of the reclaimed rubber was powdered by means of two roll mill at ambient temperature. The virgin NR was mixed with the reclaimed rubber (RR) at 60/40 ratio, and then the blends were processed with ingredients according to Table 2 on the mill for about 15 min to obtain homogeneous NR compounds. The resulting compounds was then cured at 155 °C for the optimum curing time of *t*<sub>90</sub> by compression molding.

### 2.4. Characterization

#### 2.4.1. Sol–gel measurement

In order to determine sol content of the devulcanized rubber, extraction of the soluble part was carried out using swelling method according to ASTM D 6814-02, 2002. The insoluble part was considered as gel content [28]. The mentioned method was carried out after pre-removal of the low molecular weight substance such as processing oil in the rubber. Therefore, a Soxhlet apparatus with acetone as the extraction solvent was used for at least 12 h, before swelling measurement. The obtained sample was dried to a constant weight (*m*<sub>1</sub>). Small amount of sample was immersed in toluene for 72 h in the ambient temperature. After swelling, the sample was taken out from toluene and the solvent was blotted out from the surface of sample and it was weighted instantly. Finally, the sample was placed in the oven at 80 °C to reach a constant weight (*m*<sub>2</sub>). The sol fraction (%) was calculated according to Eq. (1):

$$\text{Sol fraction (\%)} = \frac{m_1 - m_2}{m_1} \times 100 \quad (1)$$

The sol fraction is as a result of both crosslink and main chain scission showing the amount of rupture of rubber network during the process [28].

**Table 2**  
Formulations of the blends in phr.

Formulation	4-9-13
NR	60
RR	40
N660	23
oil	9
Sulfur	1
ZnO	5
Stearic acid	2
MBS	1.2
PVI	0.2
TMTD	0.3

**Table 1**  
Mechanical properties of the used NR.

Sample	CLD (10 <sup>4</sup> mol/g)	Tensile strength (MPa)	Elongation at break (%)	Density (g/cm <sup>3</sup> )
NR (115-L(SMR))	2.59	22	447	1.1

#### 2.4.2. Crosslink density

Crosslink densities of the gel part of the samples were also determined by swelling test, using Flory-Rehner equation (Eq. (2)) while the interaction parameter ( $X$ ) for toluene-NR system was adopted as 0.393 [35].

$$V_e = \frac{-[\ln(1 - V_r) + V_r + XV_r^2]}{[V_1(V_r^{1/3} - V_r/2)]} \quad (2)$$

where  $V_e$ ,  $V_r$  and  $V_1$  are crosslink density, rubber volume fraction in the swollen sample and molar volume of the solvent, respectively.

#### 2.4.3. Degree of devulcanization

The degree of devulcanization was calculated using Eq. (3):

$$\text{Devulcanization (\%)} = \frac{V_{e2} - V_{e1}}{V_{e1}} \times 100 \quad (3)$$

where  $V_{e1}$  and  $V_{e2}$  are crosslink density before and after of devulcanization, respectively. Horikx's theory was used to determine the relationship between sol fraction after degradation of network structure of the rubber and relative decrease in crosslink density. This theory was developed for further understanding the devulcanization reaction [36]. Horikx investigated two limited cases: (i) when main chain scission occurs, relative decrease in crosslink density is calculated using Eq. (4):

$$1 - \frac{v_f}{v_i} = 1 - \frac{(1 - s_2^{\frac{1}{2}})^2}{(1 - s_1^{\frac{1}{2}})^2} \quad (4)$$

where  $v_i$  and  $v_f$  are crosslink density before and after of the devulcanization.  $S_1$  and  $S_2$  are sol fraction before and after of the devulcanization, respectively. (ii) When crosslink scission occurs, relative decrease in crosslink density is calculated using Eq. (5):

$$1 - \frac{v_f}{v_i} = 1 - \frac{\gamma_f(1 - s_2^{\frac{1}{2}})^2}{\gamma_i(1 - s_1^{\frac{1}{2}})^2} \quad (5)$$

where the parameters  $\gamma_f$  and  $\gamma_i$  are the crosslink index and refer the average number of crosslinks per chain in the residual gel before and after of the devulcanization, respectively. Horikx's theory is restricted in two mention cases and could not explain the case between main chain scission and crosslink scission [37].

#### 2.4.4. Mooney viscosity and cure properties of the rubber compounds

The Mooney viscosity of the rubber compounds was measured according to ISO 289, 2005 (ML 121 °C (1 + 4) min) using a Mooney MV2000 apparatus from Alpha Technologies. The results were expressed in Mooney Units (MU).

The curing characteristics of the blends were measured according to ISO 3417, 2008 by an oscillating disk rheometer MDR 2000 from Alpha technologies at an angular displacement of  $\pm 3^\circ$  and a test frequency of 1.7 Hz. The rheometer tests were performed at 180 °C for up to 3 min.

The rate of the cure in the rubber, cure rate index (CRI), was calculated using Eq. (6):

$$\text{CRI} = \frac{100}{(t_{90} - t_{52})} \quad (6)$$

#### 2.4.5. Mechanical properties

Tensile strength, elongation at break and modulus at different elongations of the rubber vulcanizates were measured using a tensile testing machine (SANTAM STM-20, Iran) in according to ASTM-D412-68, 2002 at room temperature. Tests were carried out at speed of  $500 \pm 50$  mm/min. For each sample the average of three replicates measurements was reported.

Shore A hardness of the virgin NR and its blends was carried out using durometer hardness tester (Shore Instrument & Mfg., Co., New York) according to ASTM D 2240 at room temperature.

### 3. Results and discussion

#### 3.1. Influence of concentration of the devulcanizing agent

To investigate the effect of concentration of BPO, chemical devulcanization of NR was carried out using various amount of BPO (0, 2, 4, 6 and 8 phr) at 80 °C for 2 h. All experiments were repeated three times and average of obtained results was reported. Densities of all of the devulcanized samples were approximately  $1.1 \pm 0.1$  g/cm<sup>3</sup> (determined using digital densitometer Precisa xr-405 densitometer). Volume fraction of the rubber and percentage of the devulcanization are listed in Table 3. The corresponding sol fraction and crosslink density are shown in Fig. 1.

As the results show, volume fraction of the rubber and its crosslink density decrease with increasing the concentration of BPO up to 8 phr. Subsequently, both sol fraction and percentage of the devulcanization were increased. Breakage of weak O–O bond of BPO at 80 °C creates highly unstable radicals. These radicals or radicals generated from the primary radicals react instantly with the sulfur in the cured rubber. The higher concentration of BPO the more sulfur bonds were broken, resulting in decrease of crosslink density and consequent increase of devulcanization percentage.

The effects of BPO concentration on the sol fraction (Fig. 1) indicate that up to 4 phr the sol fraction is slowly increased. However, at higher of the concentration of BPO, the sol fraction increased sharply. Fortunately, according to Fig. 2 (Horikx theory), the crosslink bond is still broken.

A sharp decline in the crosslink density was observed with increasing the concentration of BPO up to about 6 phr. This observation confirms the effectiveness of BPO compared to the results obtained using xylene alone. The crosslink density gradually decreases as long as the concentration of BPO increased further.

As mentioned here in before, a useful tool for further understanding about reactions that occur during the devulcanization is Horikx's theory. The sol fractions of the devulcanized rubber versus decrease in crosslink density are shown in Fig. 2. All of the obtained experimental points are located on the dashed curve, under the solid curve, indicating a selective crosslink scission.

#### 3.2. Effect of reaction time

To investigate the effect of reaction time, the reaction was carried out at BPO (0, 2, 4, 6, 8, 10 phr), 80 °C and devulcanization time of 2 and 4 h. The swelling test results are depicted in Table 4 and Fig. 3.

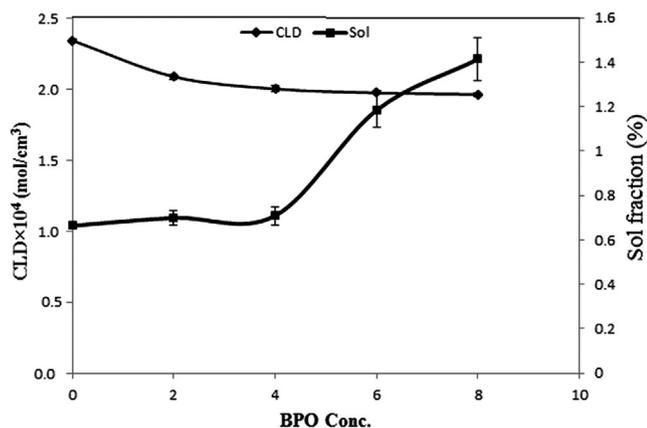
Reaction time has a major role in the chemical devulcanization that attributed to the strong reaction between the benzoyl radicals and crosslinks of the rubber. The longer the reaction time, the more of the degree of the devulcanization is achieved (Fig. 3).

As shown in Fig. 3, a linear reduction in the crosslink density was observed with addition of BPO up to about 6 phr. However, the crosslink was decreased with further addition of BPO up to 10 phr which studied. The obtained results (Table 3) can be interpreted so that at both low temperature and short time of the reaction, the

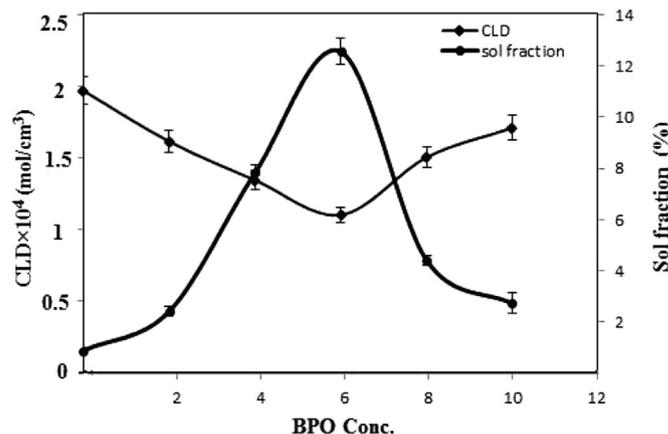
**Table 3**  
Swelling test results for the devulcanized samples.

Sample no.	Concentration of BPO (phr)	$V_r$	Standard deviation (STD)	Devulcanization (%)	Standard deviation (STD)
1	—	0.244	0.0005	9	0.23
2	2	0.232	0.0008	19	0.47
3	4	0.229	0.001	22	0.62
4	6	0.227	0.0011	23	0.69
5	8	0.226	0.0007	24	0.37

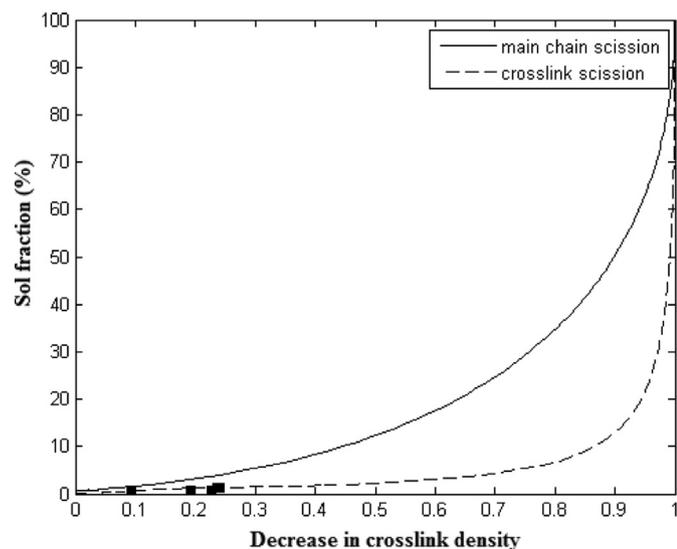
Process condition: time = 2 h, temperature = 80 °C.



**Fig. 1.** Sol fraction and crosslink density as a function of BPO concentration (Process condition: time = 2 h, temperature = 80 °C).



**Fig. 3.** Sol fraction and crosslink density as a function of BPO concentration (Process condition: time = 4 h, temperature = 80 °C).



**Fig. 2.** Sol fraction of reclaimed rubber against relative decrease in crosslink density (Process condition: time = 2 h, temperature = 80 °C); Main chain scission (solid line), crosslink scission (dash line).

**Table 4**  
Swelling test results for the devulcanized samples.

Sample no.	Concentration of BPO (phr)	$V_r$	Standard deviation (STD)	Devulcanization (%)	Standard deviation (STD)
6	—	0.227	0.0054	24	1.41
7	2	0.209	0.0024	37	0.84
8	4	0.193	0.0044	48	1.21
9	6	0.177	0.0039	57	0.84
10	8	0.202	0.0025	42	0.63
11	10	0.214	0.0025	34	0.81

Process condition: time = 4 h, temperature = 80 °C.

bonds having lower bond energy (S–S) would break (Table 5). However, at higher temperature and/or longer of the reaction time the possibility of breakage of bonds with higher bond energy (i.e., C–S and C–C) increase. As these bonds are broken, the free radicals are produced. Sometimes after scission of these bonds, recombination of some of the produced macro radicals is possible (i.e., re-crosslinking). This phenomenon known as cage effect may have led to decrease of the sol fraction.

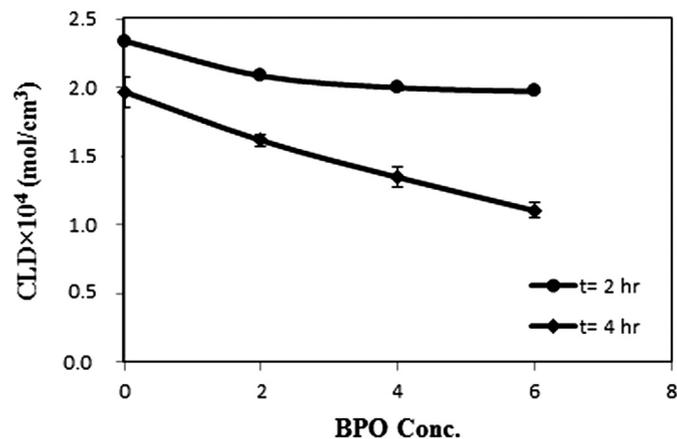
The influence of the reaction time on the degree of crosslinking using different concentrations of BPO is shown in Fig. 4. According to this Figure, crosslink density at 4 h of the reaction time was higher than the amount obtained at 2 h. Also lower crosslink density was obtained at higher the concentration of BPO.

The experimental data are also located in the Horikx's curve. As Fig. 5 shows, with increasing of the concentration of BPO, the points approach to main chain scission curve indicating that the devulcanization reaction changes to non-selective reactions. It is clear that this phenomenon is more possible in extreme conditions e.g., longer reaction time, higher temperature and higher concentration of the BPO.

In an experiment carried out using very high concentration of BPO (about 80 phr), the rubber was dispersed in the solvent after 4 h of the reaction. The obtained product was powder of the rubber indicating of high breaking down of chemical bonds in the rubber.

**Table 5**  
Bonds energies of chemical units involved in sulfur crosslinked NR [30].

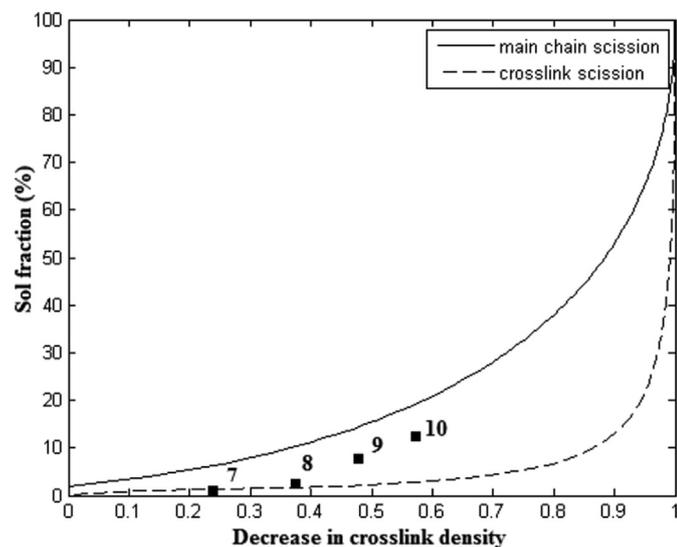
Type of bonds to be broken	Energy required (kJ/mol)
C–S	270
S–S	240
C–C	345



**Fig. 4.** Crosslink density as a function of BPO concentration at different reaction times: 2 h and 4 h.

### 3.3. Effect of temperature

In order to investigate the effect of temperature of the reaction, the chemical devulcanization of NR was carried out by means of

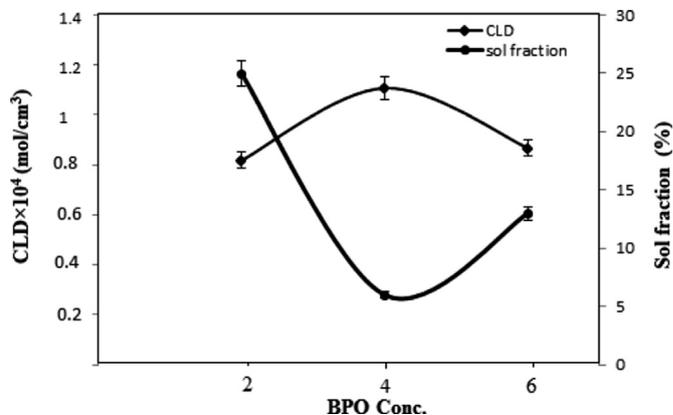


**Fig. 5.** Sol fraction of reclaimed rubber against relative decrease in crosslink density (time = 4 h,  $T = 80^\circ\text{C}$ ).

**Table 6**  
Swelling test results for the devulcanized samples.

Sample no.	Concentration of BPO (phr)	$V_r$	Standard deviation (STD)	Devulcanization (%)	Standard deviation (STD)
12	2	0.154	0.002	68	0.65
13	4	0.177	0.004	57	1.02
14	6	0.160	0.003	65	0.8

Process condition: time = 4 h, temperature =  $110^\circ\text{C}$ .



**Fig. 6.** Sol fraction and crosslink density as a function of BPO concentration (Process condition: time = 4 h, temperature =  $110^\circ\text{C}$ ).

different concentrations of BPO (2, 4 and 6 phr) in xylene at  $110^\circ\text{C}$  for 4 h. The results were indicated in Table 6 and Fig. 6.

As results shown at higher temperature and different concentrations of BPO, the crosslink density decrease and sol fraction increase more compared to lower temperature ( $80^\circ\text{C}$ ) and it is interesting that the mentioned cage effect was occurred at lower concentration of BPO (4 phr). The reaction of the devulcanization was also depicted in Fig. 7. As this Figure shows, the experimental point (no. 12) is located exactly on the solid curve, related to main chain scission. However, for the higher amount of BPO the reaction of the devulcanization took place via both main chain scission and crosslink scission.

## 4. Curing characteristic and Mooney viscosity

Curing characteristics and Mooney viscosity of the rubber compounds containing RR are given in Table 7.

Mooney viscosity of the reference compound is about 40 MU. However, adding some amount of the devulcanized rubber caused decrease in the viscosity of the compound which was beneficial to the processing of the compound. As results show, the scorch time, the time for the onset of cure, was equal for all compounds. Although optimum cure time decrease compared to the original one ( $t_{90} = 1:45$ ), the devulcanized rubber had no adverse effect on the blended compound.

### 4.1. Mechanical properties of devulcanized and revulcanized samples

Mechanical properties of the devulcanized samples (samples no: 4, 9 and 14) including tensile strength and elongation at break were measured and compared with the original sulfur crosslinked NR sample and results are depicted in Figs. 8 and 9.

Since the tensile strength is a function of the crosslink density, it is expected that the devulcanized rubber has lower tensile strength than the original one. As the benzoyl radicals break the sulfidic bonds, crosslink density decreases. So, both tensile strength and elongation at break also decrease. On the other hand, main chain

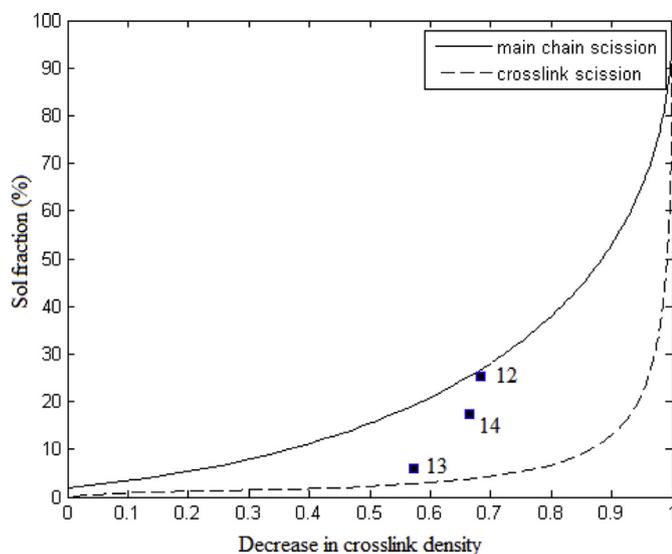


Fig. 7. Sol fraction of reclaimed rubber against relative decrease in crosslink density (time = 4 h,  $T = 110\text{ }^{\circ}\text{C}$ ).

scission causes sharp drop in the mechanical properties because of degradation of the rubber network at high reaction temperature ( $110\text{ }^{\circ}\text{C}$ ), at high concentration of BPO (higher than 6 phr) and also at high reaction time.

By comparing of the obtained results, it is concluded that the reaction temperature is the most effective parameter in the chemical devulcanization of NR using BPO. In general, chemical devulcanization of NR could be carried out in low temperatures and short reaction time without main chain scission and sharp drop of its mechanical properties.

Table 8 represents the mechanical properties of the revulcanized rubber compounds (samples no: 4, 9 and 14).

According to the results showed in Table 8, the revulcanized natural rubber have lower tensile strength and percentage of elongation at break compared to original one. The revulcanized

rubber contains certain amount of main chain degradation, which lowers the percentage of elongation and hence its tensile strength.

Among the revulcanized samples, the sample no.4 has a lower tensile strength and the percentage of elongation at break due to the lower sol content and lower the percentage of the devulcanizate. Gel fraction of the reclaimed rubber acts as “weak sites” for stress transmission to its surroundings, resulting in a lower tensile strength and elongation at break [28]. Sample no.9 and no.14 show better mechanical properties and due to near data of sol contents and the percentage of the devulcanization of these two sample, the amount of mechanical properties is approximately equal.

Hardness of all of the revulcanized samples is higher than original one possibly due to higher percentage of filler in reclaimed rubber.

Modulus of the revulcanized samples is higher than the original one. As mentioned earlier, the revulcanized rubber contains certain amount of main chain degradation, which restricted the molecular chain mobility under tension force, and hence increased its modulus [23]. It suggests that the presence of the devulcanized rubber in the blend was beneficial to the modulus of the final rubber.

## 5. Conclusions

Sulfur-cured natural rubber was devulcanized by means of benzoyl peroxide as devulcanizing agent in presence of xylene as solvent. The effect of important reclaiming parameters including temperature, time and the concentration of the devulcanizing agent were investigated. The obtained results showed that at shorter reaction time (2 h) and lower concentrations of the devulcanizing agent (2, 4, 6 and 8 phr), the devulcanization scission of crosslink bonds could be carried out selectively. However, increase of the BPO concentration, results in nonselective crosslink and backbone bond scission. Reaction time had a direct effect on the chemical devulcanization of NR led to non-selective chain and crosslink scission. Besides, recombination of the formed macro radicals might be occurred (i.e., recrosslinking) due to the cage effect. Increasing the reaction temperature also caused cage effect in lower concentration of BPO (4 phr) and severe drop in

Table 7  
Curing characteristic and Mooney viscosity of compounds.

Compound no.	Scorch time ( $t_{s2}$ ) (m:s)	Cure time ( $t_{90}$ ) (m:s)	$\Delta$ torque (dN, m)	CRI ( $\text{S}^{-1}$ )	Mooney viscosity (MU)
4	0:45	1:37	9.9	1.92	13
9	0:45	1:42	10.8	1.75	19
14	0:45	1:41	10.9	1.78	21

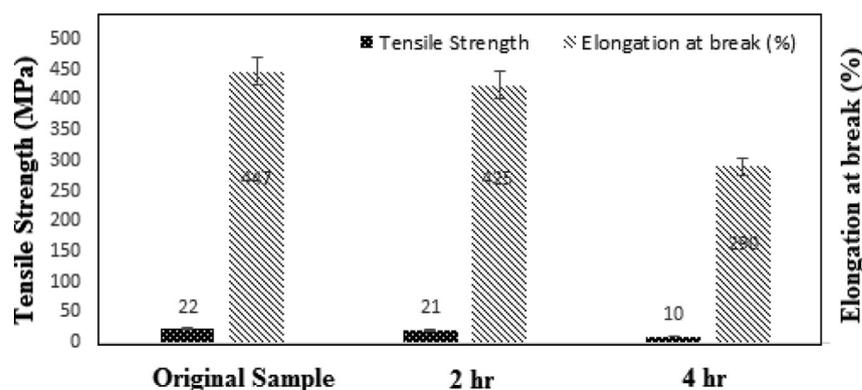


Fig. 8. Effects of the reaction time on tensile strength and elongation at break.

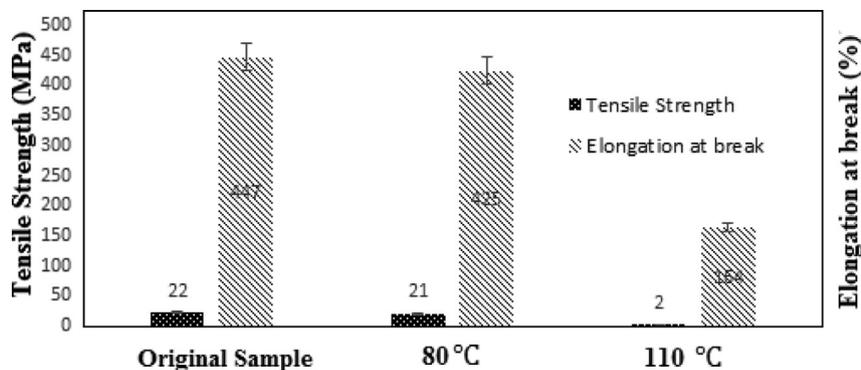


Fig. 9. Effects of the reaction temperature on tensile strength and elongation at break.

Table 8

Mechanical properties of the rubber blends.

Compound no.	Tensile strength (MPa)	Hardness (shore A)	Elongation at break (%)	Modulus at 20% (MPa)	Modulus at 50% (MPa)	Modulus at 100% (MPa)	Modulus at 200% (MPa)	Modulus at 300% (MPa)
Original	22.0	50.5	447	0.65	1.05	1.8	4.1	7.72
4	13.0	56.6	389	0.72	1.19	2.05	4.60	8.75
9	16.5	55.8	408	0.71	1.21	2.09	4.80	9.37
14	16.0	54.5	400	0.68	1.15	2.04	4.85	9.61

mechanical properties indicating significant degradation of the rubber network. Mechanical properties of the re-vulcanized samples also were determined and results showed that for the samples no. 9 and 14, the replacing 40 wt% of the virgin rubber with the devulcanized one in the blend had no adverse effect on the mechanical properties of the vulcanized rubber. The recommended reclaiming method for the chemical reclaiming of NR is a process at the optimum concentration of BPO, longer time and lower temperature. Therefore, using low quantity of the devulcanized rubber does not deteriorate the mechanical properties of the virgin rubber too much.

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